



LAWRENCE  
LIVERMORE  
NATIONAL  
LABORATORY

# Forced Volume Magnetostriction in Composite $\text{Gd}_5\text{Si}_2\text{Ge}_2$

N. Nersessian, S. W. Or, G. P. Carman, S. K. McCall,  
W. Choe, H. B. Radousky, V. K. Pecharsky, A. O.  
Pecharsky

June 1, 2004

SPIE 11th Annual International Symposium on Smart  
Structures and Materials - Active Materials: Behavior and  
Mechanics

San Diego, CA, United States

March 14, 2004 through March 18, 2004

## **Disclaimer**

---

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

## Forced Volume Magnetostriction in Composite $\text{Gd}_5\text{Si}_2\text{Ge}_2$

Nersesse Nersessian<sup>1,2a</sup>, Siu Wing Or<sup>1b</sup>, Gregory P. Carman<sup>1c</sup>, Scott K. McCall<sup>2d</sup>

Wonyoung Choe<sup>2e</sup>, Harry B. Radousky<sup>2f</sup>, Vitalij K. Pecharsky<sup>3,4g</sup>, and Alexandra O. Pecharsky<sup>3f</sup>

<sup>1</sup>Mechanical and Aerospace Department, University of California, Los Angeles

<sup>2</sup>Lawrence Livermore National Laboratory

<sup>3</sup>Ames Laboratory and <sup>4</sup>Department of Materials Science and Engineering, Iowa State University

### ABSTRACT

A  $\sim 1200$  ppm forced volume magnetostriction has been obtained in a [0-3], resin binder,  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  particulate composite. The strain is a result of a magnetically induced phase transformation from a high volume (high temperature, low magnetic field) monoclinic phase to a low volume (low temperature, high magnetic field) orthorhombic phase. The particles used in the composite were ball-milled from a bulk sample and were sieved to obtain a size distribution of  $\sim 600$  nm. Bulk  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  was manufactured via arc melting and subsequently annealed at  $1300^\circ\text{C}$  for 1 hour to produce a textured, polycrystalline sample. The transformation temperatures of the bulk sample, as measured using a Differential Scanning Calorimeter (DSC), were  $M_s = -9.3^\circ\text{C}$ ,  $M_f = -14.6^\circ\text{C}$ ,  $A_s = -4.4^\circ\text{C}$ , and  $A_f = -1.2^\circ\text{C}$ . The composite and the bulk samples were magnetically characterized using a SQUID magnetometer, and found to undergo a paramagnetic to ferromagnetic

<sup>a</sup>nersesse@ucla.edu; phone 1 310 825-9564; fax 1 310 206-2302; <sup>b</sup>swor@seas.ucla.edu; phone 1 310 825-9564; fax 1 310 206-2302; <sup>c</sup>carman@seas.ucla.edu; phone 1 310 825-6030; fax 1 310 206-2302; <sup>d</sup>mcall10@llnl.gov; phone 1 925 422-1499; fax 1 925 422-4665; <sup>e</sup>choe1@llnl.gov; phone 1 925 422-8717; fax 1 925 423-0238; <sup>f</sup>radousky1@llnl.gov; phone 1 925 422-4478; fax 1 925 423-0238; <sup>g</sup>vitkp@ameslab.gov; phone 1 515 294-8220; fax 1 515 294-9579; <sup>h</sup>pecharsky@ameslab.gov; phone 1 515 294-2728; fax 1 515 294-9579

transition during the phase transformation, consistent with published results. The bulk sample was also found to possess a maximum linear magnetostriction  $\sim 2500 \text{ ppm}$ .

**Keywords:** Volume Magnetostriction,  $\text{Gd}_5\text{Si}_2\text{Ge}_2$ , [0-3] Composites, phase transformation

## 1 INTRODUCTION

Since the discovery of the giant magnetocaloric effect ( $-\Delta S_m = \sim 36 \text{ J/kgK}$ ) near room temperature in  $\text{Gd}_5\text{Si}_2\text{Ge}_2$ ,<sup>1-2</sup> this and related  $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$  compounds have been studied extensively as these materials hold a promise for future applications in energy efficient and environmentally benign magnetic refrigeration devices.<sup>3-14</sup>  $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$  compounds also exhibit colossal volume magnetostriction due to a phase transformation.<sup>13, 15-16</sup> The volume magnetostriction can be induced thermally (spontaneous volume magnetostriction) as well as magnetically (forced volume magnetostriction), and are observed to be comparable as demonstrated by Morellon et al.<sup>13</sup> The single crystalline  $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$  compounds exhibit magnetostrictive strains up to  $\sim 10,000 \text{ ppm}$  along the crystallographic  $a$  axis. These properties make them ideal candidates for replacing materials used in actuators, such as Terfenol-D and PZT, where linear strains are limited to  $\sim 2000 \text{ ppm}$  and volume strains are close to zero.<sup>17</sup>

One problem with magnetic actuators is eddy current losses when actuated at high frequencies.<sup>18</sup> Eddy current losses significantly limit bandwidth with typical values less than  $1 \text{ kHz}$ . A solution to

this problem is to embed the magnetic particles in a non-conducting binder (i.e. create a composite). The smaller particle sizes substantially reduce eddy currents without lowering the strain significantly.<sup>18</sup> Characteristic frequency (an indicator of eddy current losses) becomes larger with decreasing eddy currents, typically increasing by two orders of magnitude as the particles size is reduced ten-fold.

In this study, we report the magnetic characteristics of a 0-3, resin binder,  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  particulate composite. The forced volume magnetostriction is measured using two orthogonal strain gages and compared to forced volume magnetostriction measured in polycrystalline bulk  $\text{Gd}_5\text{Si}_2\text{Ge}_2$ . An analytical model is also developed based on a rule of mixtures formulation providing a comparison between theoretical values and experimental results for the magnetically strain in the  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  particulate composite.

## **2 MANUFACTURING AND TESTING**

Bulk, polycrystalline,  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  was manufactured by arc-melting 99.99 wt.% pure Gadolinium, and 99.99 wt.% Silicon and Germanium. X-ray Diffraction (XRD) measurements confirmed the material to posses the monoclinic  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  type structure at room temperature. Deferential Scanning Calorimeter (DSC) measurements indicate the following transformation temperatures: Martensite Start ( $M_s$ ) =  $-9.3^\circ\text{C}$ , Martensite Finish ( $M_f$ ) =  $-14.6^\circ\text{C}$ , Austenite Start ( $A_s$ ) =  $-4.4^\circ\text{C}$ , and

Austenite Finish ( $A_f$ ) = 1.2°C. Bulk  $Gd_5Si_2Ge_2$  was then squared up by Electron Discharge Machining (EDM) to obtain, a single smooth plane for magnetostriction measurements.

Particulate used to make the composite was obtained by ball-milling the bulk material for 5-30 seconds in air. Particulate obtained was random in shape and was sieved to get a particle size distribution of  $\leq 600\mu m$ . DSC measurements indicate the following transformation temperatures for the ball-milled particles:  $M_s = -6.9^\circ C$ ,  $M_f = -14.6^\circ C$ ,  $A_s = -6.7^\circ C$ , and  $A_f = -0.36^\circ C$ . Little oxidation was expected due to the short ball milling duration. Nevertheless, DSC measurements indicate a less pronounced peak during the phase transformation suggesting that the particles were somehow damaged during the ball milling process.

Figure 1 is a picture of a [0-3], polymer-bonded, 35% volume fraction  $Gd_5Si_2Ge_2$  particulate composite. The composite was obtained by first mixing the  $Gd_5Si_2Ge_2$  particulate with a vinyl ester resin (Dow Derakane 411-C50), and subsequently de-gassing to eliminate occurrence of voids in the cured composite. The particulate was then aligned under a static magnetic field of  $\sim 150kA/m$  using a pair of Nd-Fe-B permanent magnets.<sup>19</sup> Alignment, however, is expected to be poor due to the  $Gd_5Si_2Ge_2$  being paramagnetic at room temperature. The mixture was cured at room temperature for 1 hour after which it was cured for an additional 4 hours in an oven at 70°C. The cured composite was finally de-molded and lapped to  $1.5 \times 1.5 \times 1.5 \text{ cm}^3$ .

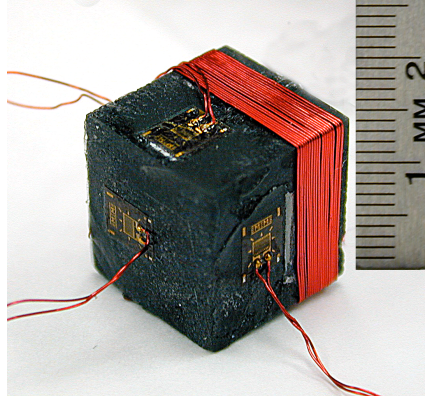


Figure1: Composite  $\text{Gd}_5\text{Si}_2\text{Ge}_2$

Magnetization measurements were conducted on bulk  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  and on a 35% volume fraction  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  composite using a SQUID magnetometer. Magnetostriction measurements were performed using a Quantum Design 9T physical property measurement system (PPMS). Two orthogonal Micro-Measurement EA-06-031CF-120 strain gages were used to measure the magnetostriction in the composite, while a single strain gage was used to measure the magnetostriction in the bulk material. In both cases a blank strain gage was used to compensate for the effect of the applied magnetic field on the strain gage.

### 3 RESULTS

#### 3.1 Bulk $\text{Gd}_5\text{Si}_2\text{Ge}_2$

Figure 2 is a plot of magnetization (M) vs. applied magnetic field (H) in bulk  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  at various constant temperatures (-16 °C, -6 °C, 4 °C, 9 °C, 14 °C, 19 °C, 24 °C, and 44 °C). The plot shows the

paramagnetic to ferromagnetic transition by the large jump in magnetization ( $\sim 0.3 \rightarrow 0.9T$ ) at certain constant temperatures (i.e. 9 °C, 14 °C, 19 °C, and 24 °C). This jump in magnetization (i.e. paramagnetic to ferromagnetic transition) shifts to higher magnetic field values, from  $\sim 2000$  kA/m to  $\sim 4000$  kA/m, as the temperature is increased (i.e 9 °C to 24 °C). To understand this we must know that the magnetic structure of  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  is determined by the thermal energy that tends to disorder the magnetic moments and the exchange interaction between the Gd atoms that tends to order the magnetic moments (Levin, 2001). At a certain magnetic field range the exchange interaction energy becomes larger than the thermal energy and the material transforms from the paramagnetic to ferromagnetic state. Therefore, by increasing the temperature this balance in energy is shifted to higher magnetic field levels due to the increase in thermal energy, resulting in an increase in the magnetic level at which the transformation occurs.

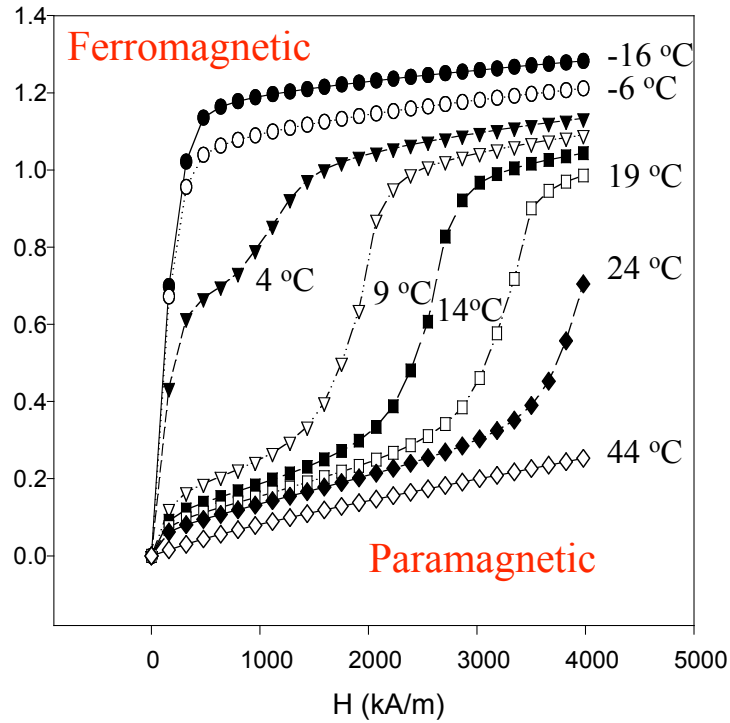


Figure 2: Behavior of magnetization as a function of applied magnetic field in bulk  $\text{Gd}_5\text{Si}_2\text{Ge}_2$



Figure 3 is a plot of the strain (parallel to the direction of magnetization) vs. temperature for the bulk  $\text{Gd}_5\text{Si}_2\text{Ge}_2$ . The figure shows a large increase in the linear strain ( $\sim 0.2\%$ ) during the phase transformation after which there is a continued increase in the strain upon increasing the applied magnetic field. The large jump in strain occurs at higher magnetic field levels as the temperature is increased agreeing well with the magnetization data (Figure 2). Also, a larger jump in strain occurs at higher temperatures suggesting that along the measurement axis the contraction increases as the temperature is increased. The largest jump in linear strain of 2500ppm occurs at a temperature of 22 °C. This strain is comparable to that exhibited by the  $\text{RFe}_2$  (where R stands for rare earth) magnetostrictive alloys (e.g.  $\text{TbFe}_2$ ).

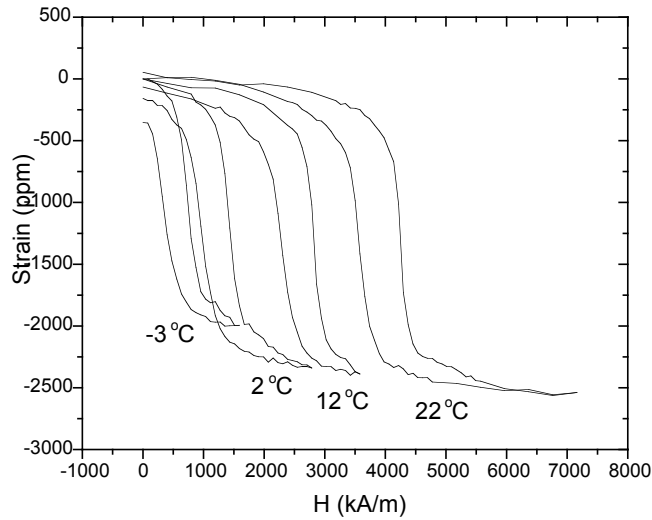


Figure 3: Linear magnetostriction in bulk  $\text{Gd}_5\text{Si}_2\text{Ge}_2$

### 3.2 Composite $\text{Gd}_5\text{Si}_2\text{Ge}_2$

Figure 4 is a plot of magnetization ( $M$ ) vs. applied magnetic field ( $H$ ) in composite  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  at various constant temperatures ( $-13^\circ\text{C}$ ,  $3^\circ\text{C}$ ,  $7^\circ\text{C}$ ,  $17^\circ\text{C}$ , and  $27^\circ\text{C}$ ). The plot shows the magnetization saturating at  $\sim 0.45\text{ T}$ , which scales well with the saturation magnetization of  $\sim 1.3\text{ T}$  for the bulk  $\text{Gd}_5\text{Si}_2\text{Ge}_2$ . The plot shows a similar paramagnetic to ferromagnetic transition as for the bulk (Figure 2) by the large jump in magnetization ( $\sim 0.1 \text{--} 0.3\text{ T}$ ) at various constant temperatures (i.e.  $-3^\circ\text{C}$ ,  $7^\circ\text{C}$ , and  $17^\circ\text{C}$ ). The trend is similar to the bulk  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  whereby the jump in magnetization (i.e. paramagnetic to ferromagnetic transition) shifts to higher magnetic field values as the temperature is increased.

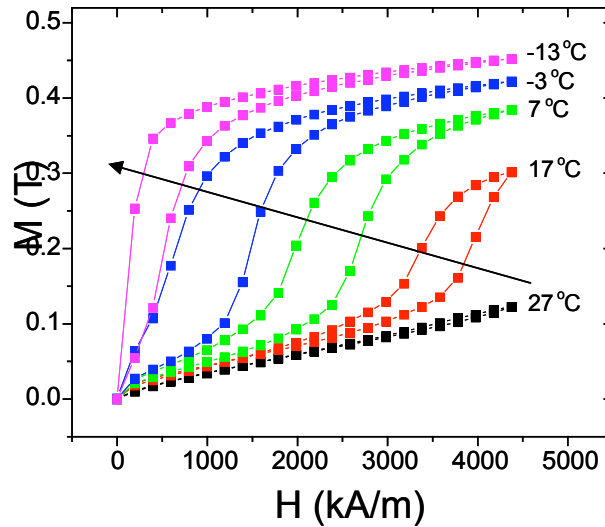


Figure 4: Behavior of magnetization as a function of applied magnetic field in composite  $\text{Gd}_5\text{Si}_2\text{Ge}_2$

Figure 5 is a plot of (a) the strain (parallel and perpendicular to the direction of magnetization) vs. magnetic field (T) at  $-3^{\circ}\text{C}$  and (b) the parallel strain vs. magnetic field at various temperatures ( $-3^{\circ}\text{C}$ ,  $7^{\circ}\text{C}$ ,  $17^{\circ}\text{C}$ , and  $27^{\circ}\text{C}$ ) for the composite  $\text{Gd}_5\text{Si}_2\text{Ge}_2$ . Figure 5(a) shows the strain measured along the direction of magnetization ( $\epsilon_{\parallel}$ ) and strain measured perpendicular to the direction of magnetization ( $\epsilon_{\perp}$ ) at  $-3^{\circ}\text{C}$ . Saturation strains measured along both directions ( $\sim 500\text{ppm}$  and  $\sim 350\text{ppm}$ ) are significantly lower than those measured in bulk  $\text{Gd}_5\text{Si}_2\text{Ge}_2$ . There are two possible explanations for these. One possible explanation is that the particles were damaged during the ball milling process as supported by the DSC data. A second possible explanation is the random orientation of the  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  particles in the polymer matrix due to the poor alignment of the particles during cure. Essentially, there are two types of polymer-bonded composites, e.g. a 0-3 (particles dispersed randomly in a polymer matrix) and a 1-3 (particles aligned in a single direction in a polymer matrix) composite. It is well known that an aligned 1-3 composite exhibits a significantly higher strain than a randomly dispersed 0-3 composite.<sup>21</sup> A 0-3 composite was obtained in our case as a result of the particles being paramagnetic at room temperature, and therefore impossible to align under moderate magnetic fields. Aligning at the low temperature ferromagnetic phase was also not possible due to the temperature required to cure the epoxy.

Figure 5(b) shows the strain measured along the direction of magnetization ( $\epsilon_{\parallel}$ ) and strain measured perpendicular to the direction of magnetization ( $\epsilon_{\perp}$ ) at  $-3^{\circ}\text{C}$ ,  $7^{\circ}\text{C}$ ,  $17^{\circ}\text{C}$ , and  $27^{\circ}\text{C}$ . The plot shows the large jump in negative strain during the phase transformation decreasing as the temperature is increased. Furthermore, the negative strain decreases with increasing magnetic field

beyond the phase transformation. This is opposite to magnetostrictive strains observed in the bulk  $\text{Gd}_5\text{Si}_2\text{Ge}_2$ , whereby the negative strain increased with increasing temperature.

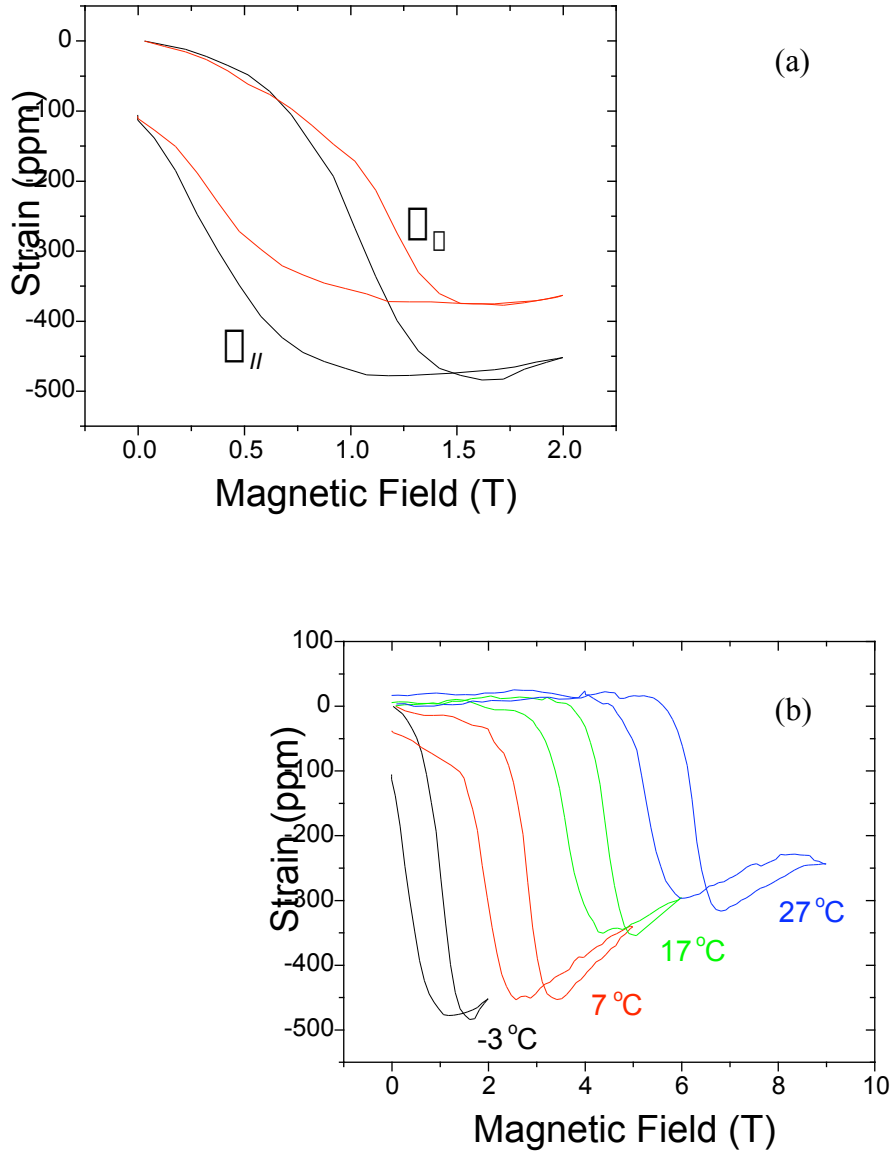


Figure 5: (a) Parallel and perpendicular magnetostriction at  $-3^\circ\text{C}$  and (b) parallel magnetostriction at various constant temperatures in composite  $\text{Gd}_5\text{Si}_2\text{Ge}_2$

Knowing the strains parallel and perpendicular to the direction of magnetization and assuming the composite to be isotropic the volume magnetostriction can be calculated using the following formula:

$$\Delta = \Delta_{//} + 2\Delta_{\perp}. \quad (1)$$

Figure 6 is a plot of forced volume magnetostriction ( $\Delta$ ) as a function of temperature for composite  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  using data shown in Figure 5. The plot shows the volume magnetostriction in the composite generally decreasing as the temperature is increased from  $-3^\circ\text{C}$  to  $27^\circ\text{C}$ . This trend is different than that observed in the bulk  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  and can be partially attributed to the softening of the matrix at increased temperatures. The other reason is that the ball milling process damages the particles in the form of oxidation, thereby altering their properties, which would explain the difference in properties between the bulk sample and the composite.

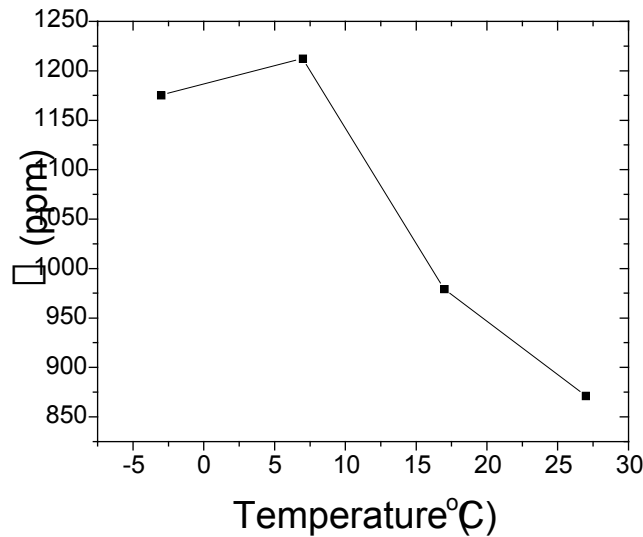


Figure 6: Volume magnetostriction in composite  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  as a function of temperature

## CONCLUSION

In summary, bulk, polycrystalline  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  was manufactured via arc-melting and its transformation temperatures determined by DSC measurements. The bulk material was also ball milled and its transformation temperatures determined. Comparison of the DSC measurements of the bulk and ball milled particles suggest that the particles were damaged during the ball milling process possible due to oxidation. The bulk  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  was magnetically characterized using a SQUID magnetometer showing the jump in magnetization during the paramagnetic to ferromagnetic transition accompanying the phase transformation. The transformation occurring at higher magnetic fields with increased temperature was attributed to the interplay between the exchange interaction energy between the Gd atoms and the thermal energy, the latter becoming larger as the temperature is increased. A polymer-bonded, 35% volume fraction, [0-3]  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  composite was also manufactured. Magnetic properties exhibited a similar trend as for the bulk with an appropriate scaling of the magnetization. Magnetostriction measurements of the bulk material and the composite indicate a significant reduction in the linear magnetostriction in the composite ( $\sim 500$  ppm) as compared to the bulk ( $\sim 2500$  ppm). The reduction was attributed to 1) the stiffness of the vinyl ester matrix and 2) the [0-3] alignment of the particles in the  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  composite.

## ACKNOWLEDGEMENTS

The authors of this paper gratefully acknowledge LLNL and the ONR (MURI) program (FSMA) for their support. Work at LLNL was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract number W-7405-ENG-48. Work at Ames Laboratory was performed under the auspices of the Office of Basic Energy Sciences, Materials Sciences Division of the US Department of Energy under contract number W-7405-ENG-82 with Iowa State University.

## REFERENCES

- <sup>1</sup> V. K. Pecharsky, K. A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1997).
- <sup>2</sup> V. K. Pecharsky, K. A. Gschneidner, Jr., Appl. Phys. Lett. **70**, 3299 (1997).
- <sup>3</sup> J. Glanz, Science **279**, 2045 (1998).
- <sup>4</sup> C. B. Zimmer, Adv. Cryog. Eng. **43**, 1759 (1998).
- <sup>5</sup> V. K. Pecharsky, K. A. Gschneidner, Jr., J. Magn. Magn. Mater. **200**, 44 (1999)
- <sup>6</sup> W. Choe, V. K. Pecharsky, A.O. Pecharsky, K. A. Gschneidner Jr., V. G. Young Jr., and G. J. Miller, Phys. Rev. Lett. **84**, 4716 (2000).
- <sup>7</sup> K. A. Gschneidner, Jr., V. K. Pecharsky, E. Brück, H. G. M. Duijin, E. M. Levin, Phys. Rev. Lett. **85**, 1490 (2000)
- <sup>8</sup> A. Giguere, M. Foldeaki, B. R. Gopal, R. Chahine, T. K. Bose, A. Frydman, J. A. Barclay, Phys. Rev. Lett. **83**, 2262, 1999.

- <sup>9</sup> J. Meyers, S. Chumbley, W. Choe, G. J. Miller, Phys. Rev. B **66**, 012106 (2002)
- <sup>10</sup> F. Casanova, X. Battle, A. Labarta, J. Marcos, L. Manosa, A. Planes, Phys. Rev. B **66**, 100401 (2002)
- <sup>11</sup> A. O. Pecharsky, K. A. Gschneidner Jr., V. K. Pecharsky, J. Appl. Phys. **93**, 4722, (2003)
- <sup>12</sup> W. Choe, G. J. Miller, J. Meyers, S. Chumbley, A. O. Pecharsky, Chem. Mater. **15**, 1413 (2003).
- <sup>13</sup> For a review on  $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ , see V. K. Pecharsky, K. A. Gschneidner, Jr., Adv. Mater. **13**, 683 (2001).
- <sup>14</sup> see <http://www.external.ameslab.gov/News/release/2001rel/01magneticrefrig.htm>
- <sup>15</sup> L. Morellón, P.A. Algarabel, M.R. Ibarra, J. Blasco, and B. Garcia-Landa, Phys. Rev. B **58**, R14721 (1998).
- <sup>16</sup> A. del Moral, P. A. Algarabel, J. I. Arnaudas, L. Benito, M. Ciria, C. de la Fuente, B. Garcia-Landa, M. R. Ibarra, C. Marquina, L. Morellón, J. M. de Teresa, J. Magn. Magn. Mater. **242-245** 788 (2002).
- <sup>17</sup> A. E. Clark, in Handbook on the Physics and Chemistry of Rare Earths Vol 2(Eds:K. A. Gschneidner Jr., L. R. Eyring), North-Holland, 1979, Ch 15.
- <sup>18</sup> A.E. Clark, U.S. Patent No. 4,378,258, March 29 (1983).
- <sup>19</sup> S.W. Or, N. Nersessian, and G.P. Carman, J. Magn. Magn. Mater. **262**, L181 (2003).
- <sup>20</sup> E.M. Levin, K.A. Gschneidner Jr., and V.K. Pecharsky, J. Magn. Magn. Mater. **231**, 135 (2001).
- <sup>21</sup> T.A. Duenas and G.P. Carman, J. Appl. Phys. **90**, 2433 (2001).